JOURNAL OF MATERIALS SCIENCE 26 (1991) 5292–5296

Synthesis of polycrystalline alumina fibre with aluminium chelate precursor

T. YOGO, H. IWAHARA
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

Polycrystalline alumina fibre was successfully synthesized by pyrolysis of preceramic fibre formed from aluminium chelate compound. Ethyl 3-oxobutanoatodiisopropoxyaluminium (EOPA) was reacted with glacial acetic acid yielding a polymeric product. The absorption bands ascribed to Al–O from 630–705 cm^{-1} changed from a sharp to a broad band on treatment with acetic acid. The ^{13}C NMR spectrum of EOPA changed from sharp singlets to multiplets after the reaction with acetic acid. The viscosity of the polymeric product increased in intensity with increasing amount of acetic acid. The viscosity of the polymeric product formed from EOPA–30 mol % acetic acid was 450 Pa s at 30 °C, and decreased to 5.4 Pa s with increasing measurement temperature from 30–70 °C. The ^{27}Al resonance at 35 p.p.m. increased in intensity with increasing viscosity of the polymeric precursor. The molecular weight of the precursor was distributed from 400–800. The polymeric precursor pyrolysed at 500 °C in air was amorphous to X-rays, and crystallized in γ-alumina at 840 °C. The precursor fibres were pyrolysed, to yield fine-grained fibres of α-alumina, at 1300 °C for 1 h.

1. Introduction

Fibre-reinforced materials have received increased attention and are growing in application in the field of composites materials. Alumina and modified alumina fibres are used for temperature-resistant fibres.

A chemical technique has been used for the synthesis of the ceramic fibre precursor, because refractory oxides have extremely high melting points, as well as a low viscosity of melts. Alumina and modified alumina fibres have been fabricated using a sol–gel process. The precursor fibre was spun from a viscous sol prepared by the hydrolysis of aluminium compounds, such as aluminium acetate [1, 2], oxychloride [3], chloride [4], alkoxide [5] and diethylaluminium derivatives [6]. The aqueous solution containing aluminium compounds was condensed and/or polymerized until an appropriate viscosity for spinning was reached. Organic additives were used to raise the viscosity of the solutions and to improve the spinning characteristics.

Usually, the spinning conditions are critical in the sol–gel process, because the viscosity of the sol changes with time, and increases very rapidly once the formation of cross-linkages starts. On the other hand, the time-independent viscosity of starting polymer is one of the most distinct differences from the sol–gel process.

This paper describes the synthesis of alumina fibre from aluminium chelate compound. The polymeric precursor was synthesized by the reaction of aluminium diketonato compound with glacial acetic acid without the addition of water for hydrolysis. The polymeric precursor was analysed by infrared spectroscopy ^{13}C, ^{27}Al nuclear magnetic resonance (NMR) and mass spectroscopy (MS). The viscosity of the precursor was investigated using a rotational viscometer. Crack-free α-alumina fibres were prepared from the precursor fibres, which were spun from the polymeric aluminium chelate compound.

2. Experimental procedure

2.1. Starting materials

Ethyl 3-oxobutanoatodiisopropoxyaluminium, $Al(O^iC_3H_7)_2(CH_3COCHCOOC_2H_5)$, (EOPA) was prepared as given by Patterson *et al.* [7].

2.2. Synthesis of alumina

The following procedure for the synthesis of Al_2O_3 is representative. The procedure for the synthesis of the precursor was carried out under nitrogen without any solvent.

0.90 g glacial acetic acid (15 mmol) was added dropwise to 13.7 g ethyl 3-oxobutanoatodiisopropoxyaluminium (50 mmol), and then the reaction mixture was refluxed at 190 °C for 2 h to give a pale yellow transparent liquid. Volatile components were removed from the reaction product *in vacuo* yielding a viscous liquid.

The resultant product was pyrolysed in air from room temperature to 500 °C at 1 °C min^{-1}. The pyrolysis product was heat treated at temperatures between 800 and 1300 °C for 1 h.

The precursor was melted in a brass extruder above 80 °C, and then extruded through the spinneret, of

0022–2461/91 $03.00 + .12

diameter 300 μm, below 60 °C. The precursor fibre was also spun from the bulk precursor using a glass rod. The precursor fibre was dried at room temperature, and then fired from room temperature to 600 °C at 0.2 °C min^{-1} in air. The ceramic fibre was subsequently heat treated at temperatures from 800–1300 °C for 1 h.

2.3. Characterization of products

The organic product was characterized using infrared and NMR spectra. Infrared spectra of products were measured by the liquid film method with KBr discs. ^{13}C NMR spectra were measured in $CDCl_3$ solution using tetramethylsilane as an internal standard. ^{27}Al NMR spectra were measured at 65.18 MHz using a Bruker AC250 spectrometer. The spectra were recorded in $CDCl_3$ solution with $Al(H_2O)_6^{3+}$ as an external standard. The volatile components, as reaction by-products, were analysed by gas chromatography (GC). Molecular weights were determined cryoscopically using benzene as a solvent, and with field desorption mass spectroscopy (FDMS). The viscosity of the precursor was measured by a rotational viscometer using a cone-and-plate and a spindle, respectively, depending upon the magnitude of viscosity, from 30–70 °C. The burn-out and crystallization behaviour of polymeric precursor were measured using differential thermal analysis–thermogravimetry (DTA–TG) at a heating rate of 10 °C min^{-1}.

The pyrolysis product was analysed by X-ray diffraction analysis (XRD) with CuK_α radiation and scanning electron microscopy (SEM).

3. Results and discussion

3.1. Synthesis and characterization of polymeric organoaluminium compound

3.1.1. Synthesis of polymeric organoaluminium compound

Ethyl 3-oxobutanoatodiisopropoxyaluminium (EOPA) was reacted with glacial acetic acid affording precursors for alumina. No water was used for the synthesis of precursors in order to prevent the gelation of products.

The polymeric product synthesized from EOPA and acetic acid was a transparent, viscous liquid and soluble in usual organic solvents, such as benzene and chloroform.

3.1.2. Infrared spectroscopy

The infrared spectra of the starting EOPA and its reaction products with 5 mol % AcOH are shown in Fig. 1. The absorption bands of the Al–O bond at 630 and 705 cm^{-1} [8, 9] in the starting EOPA (Fig. 1a) changed from separate to coalesced bands after polymerization, as shown in Fig. 1b. This change suggests the formation of a product with various kinds of Al–O bonds from the starting single compound. The absorption bands ascribed to ethyl 3-oxobutanoato ligands at 1620, 1570 and 1530 cm^{-1} [9] were observed in both compounds.

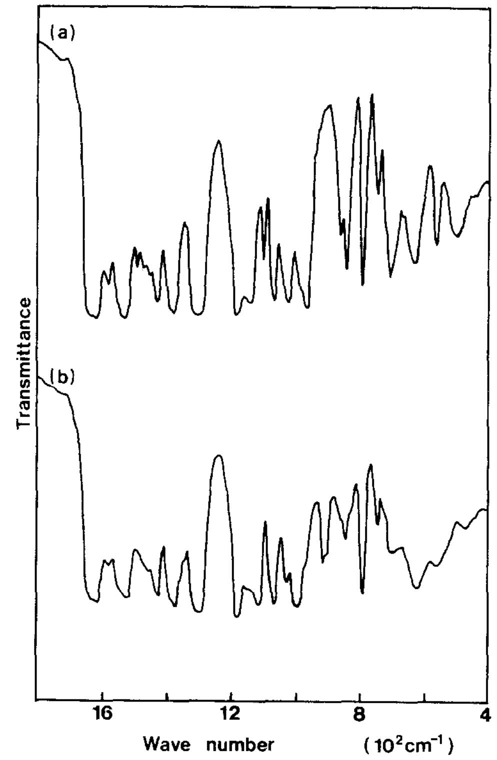


Figure 1 Infrared spectra of starting aluminium compound and polymeric product. (a) Ethyl 3-oxobutanoatodiisopropoxyaluminium (EOPA); (b) polymeric product formed from EOPA-5 mol % acetic acid.

3.1.3. ^{13}C NMR spectroscopy

The ^{13}C NMR spectra of products reacted with various amounts of acetic acid from 5.0–30 mol % are shown in Fig. 2. The signals of the starting EOPA in Fig. 2a were assigned as follows: $\delta =$ 14.4 p.p.m. ($CH_3COCHCOOCH_2\mathit{C}H_3$), multiplet from 22–28 p.p.m. ($\mathit{C}H_3COCHCOOCH_2CH_3$ and $(\mathit{C}H_3)_2CHO$), multiplet from 56–68 p.p.m. ($CH_3COCHCOO\mathit{C}H_2CH_3$ and $(CH_3)_2\mathit{C}HO$), 86.0 p.p.m. ($CH_3CO\mathit{C}HCOOC_2H_5$), 174.9 p.p.m. ($CH_3COCH\mathit{C}OOC_2H_5$), 187.1 p.p.m. ($CH_3\mathit{C}OCHCOOC_2H_5$). The figure at the top of the signal in Fig. 2 corresponds to the figure on each carbon of the molecular structure. The assignment of signals is in accordance with Breitmaier and Voelter [10].

The signals of ethyl 3-oxobutanoato ligands changed from sharp to diffused lines numbered 3, 4 and 5 as shown in Fig. 2b after the reaction of EOPA with acetic acid. The multiplet of these signals results from various kinds of carbon having a slightly different chemical environment from each other.

The decrease in isopropyl carbons at 27 and 66 p.p.m. (arrowed in Fig. 2) in intensity from Fig. 2a to Fig. 2c shows the increased amount of eliminated isopropyl groups from EOPA with increasing amount of acetic acid. Therefore, acetic acid eliminates the isopropoxy group from EOPA. However, the product formed from EOPA–30 mol % AcOH still had the isopropyl group as shown in Fig. 2c.

3.1.4. ^{27}Al NMR spectroscopy

The ^{27}Al NMR spectrum of the polymeric precursor formed from EOPA was measured in order to investigate the coordination of the aluminium atom.

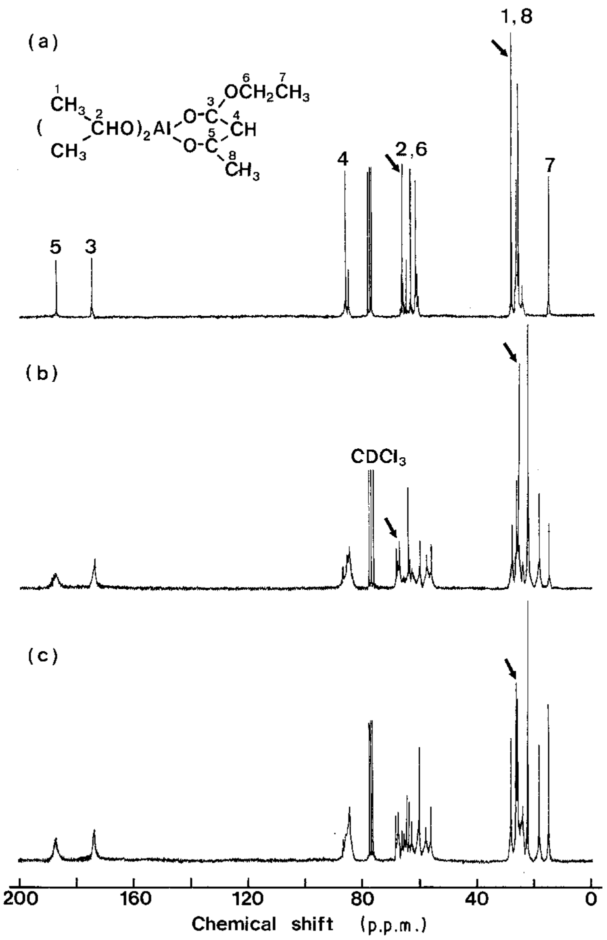


Figure 2 ^{13}C NMR spectra of polymeric product synthesized from EOPA and various amounts of acetic acid. (a) Starting EOPA; (b) product formed from EOPA and 5 mol % AcOH; (c) product formed from EOPA and 30 mol % AcOH.

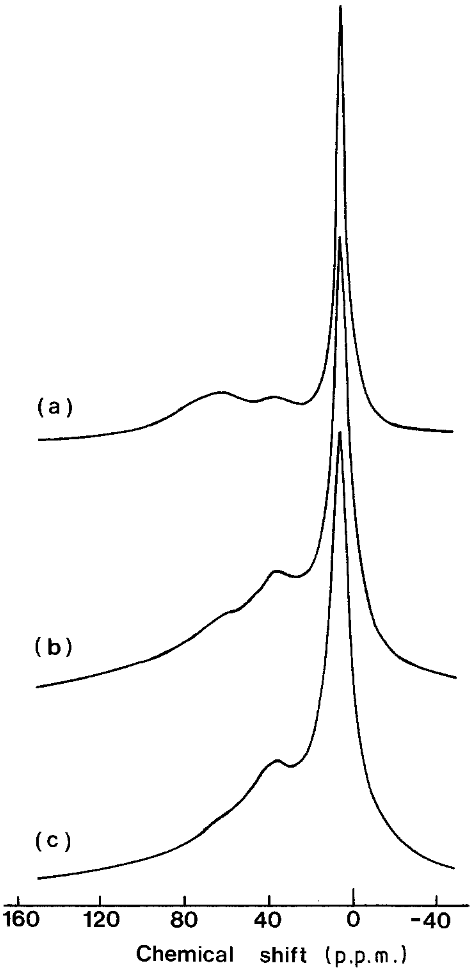


Figure 3 Change of ^{27}Al NMR spectra of polymeric precursor with the amount of acetic acid. (a) Starting EOPA; (b) product formed from EOPA and 5 mol % AcOH; (c) product formed from EOPA and 50 mol % AcOH.

The spectra of the starting EOPA and its reaction products with acetic acid are shown in Fig. 3. The starting EOPA has four-coordinated aluminium centered at 62 p.p.m. [11]. The signal at 35 p.p.m. can tentatively be ascribed to five-coordinated aluminium, because five-coordination results in a substantial upfield shift to four-coordination [12]. The strong resonance at 4.2 p.p.m. is due to the six-fold coordination of aluminium–oxygen octahedra [13, 14]. On the basis of these results, EOPA becomes associated, affording dimers in $CDCl_3$ solution as reported for aluminium alkoxide itself [12].

The signal at 4.2 p.p.m. in the starting EOPA increased in half-value width on reaction with acetic acid from Fig. 2a to Fig. 2b. The decrease in symmetry and the increase in distortion around the octahedrally co-ordinated aluminium are responsible for the broadening of the signal [15]. The signal at 35 p.p.m. increased in intensity after treatment with 5 mol % acetic acid as shown in Fig. 3b. The steric and electronic environment of the aluminium atom changed, raising the intensity of the signal at 35 p.p.m. between the region of four- and six-coordinated aluminium atoms. When EOPA was reacted with 50 mol % acetic acid, the four-coordinated aluminium at 62 p.p.m. almost disappeared in the broad signal centred at 35 p.p.m. as shown in Fig. 3c. The reaction of EOPA with acetic acid changes the coordination around the aluminium atom, and increases the amount of higher coordinated aluminium atom rather than that of the starting EOPA.

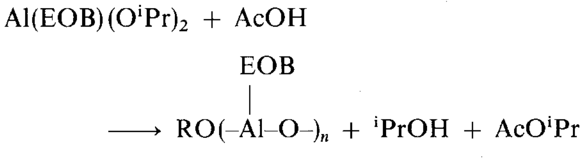
3.1.5. Molecular weight

The starting EOPA is dimeric in benzene, because the molecular weight of EOPA was 550 ± 30 (calculated for EOPA, 274.3) with cryoscopic measurements in benzene. The molecular weight of the polymeric product increased from 588 to 790 when the molar per cent of acetic acid was raised from 2.5 to 30 mol %.

The product formed from EOPA and 30 mol % acetic acid was analysed by FDMS. The mass of the product has the distribution centred at 400 and 600, respectively. Therefore, the product mainly consists of dimers and trimers.

3.1.6. Structure of polymeric product

The reaction between EOPA and acetic acid is considered to proceed as shown in Equation 1.



$$\mathrm{Al(EOB)(O^iPr)_2 + AcOH} \longrightarrow \mathrm{RO(\!-\!\overset{\overset{EOB}{|}}{Al}\!-\!O\!-\!)_n + {}^iPrOH + AcO^iPr} \qquad (1)$$

The formation of isopropyl alcohol (^{i}PrOH) and isopropyl acetate (AcO^{i}Pr) as low-boiling components were confirmed by ^{13}C NMR and GC.

The polymeric product has ethyl 3-oxobutanoato (EOB) ligands on the basis of infrared and ^{13}C NMR spectroscopy. Because EOB is a bidentate ligand, the oligomers in the polymeric product can have a structure unit of $(\text{-Al(EOB)}_2\text{-O-})$, which includes octahedrally coordinated aluminium. A mixture of $(\text{RO})_{3-n}\text{Al(EOB)}_n$ ($n < 3$) appears to constitute the low molecular weight components less than 500. The polymeric product consists mainly of monomeric chelate compounds and their oligomers.

3.2. Viscosity and spinnability of polymeric precursor

The product formed from EOPA and glacial acetic acid had a time-independent and stable viscosity.

The change in viscosity with the amount of acetic acid is shown in Fig. 4. The viscosity at 75 °C is plotted against the shear rate in Fig. 4. The viscosity of the starting EOPA was of the order of 10^{-2} Pa s. The viscosity increased by one order of magnitude on treatment with only 2.5 mol % acetic acid, and then continued to increase on increasing the amount of acetic acid from 5.0 to 30 mol %. The increase in viscosity is attributable to the increase in molecular weight. In addition, the viscosity of the product increases by the formation of intra- and intermolecular coordination, which increase the coordination number of the aluminium atom, as shown in Fig. 3.

The viscosity of the polymeric precursor formed from EOPA and 30 mol % acetic acid is dependent upon the measurement temperature, as shown in Fig. 5. The shear rate for the measurement was $1.9\ \text{s}^{-1}$. The viscosity decreased in magnitude from 450 Pa s (4500 P) to 5.4 Pa s (54 P) on increasing the measurement temperature from 30 to 70 °C.

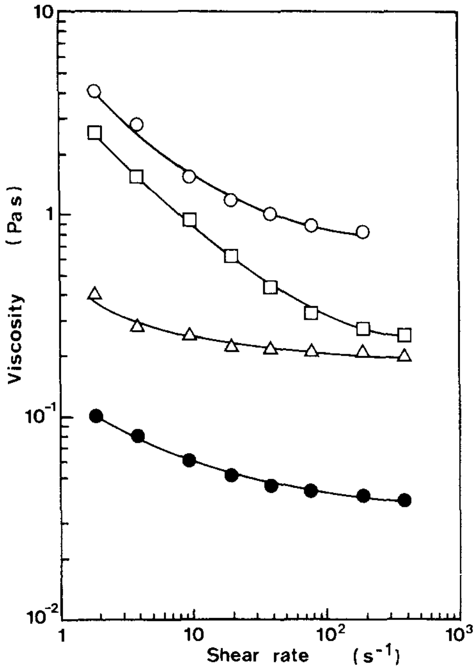


Figure 4 Change of viscosity for polymeric precursor with the amount of acetic acid and shear rate at 75 °C. (●) Starting EOPA, (△) EOPA–2.5 mol % AcOH, (□) EOPA–5 mol % AcOH, (○) EOPA–30 mol % AcOH.

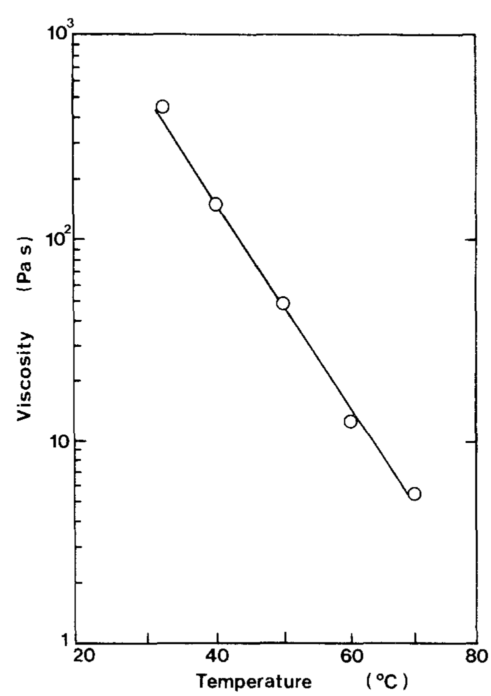


Figure 5 Variation of viscosity for precursor formed from EOPA–30 mol % AcOH with measurement temperatures from 30–70 °C at shear rate of $1.9\ \text{s}^{-1}$.

The precursor formed from EOPA and 30 mol % acetic acid was extruded through a spinneret into a fibrous shape. The viscosity of the present precursor suitable for extrusion was found to be around 10^2 Pa s in Fig. 5. The working temperature for extrusion was 30–50 °C. The length of fibre was as long as 80 cm, which was the height of extruder tip from a floor.

3.3. Synthesis of alumina from organoaluminium precursor

3.3.1. *Crystallization process*

The polymeric precursor was pyrolysed in air from room temperature to 500 °C yielding a greyish white solid in a yield of 23% by weight. Then, the product was heat treated at temperatures between 800 and 1300 °C for 1 h in air.

The XRD profiles of the products are shown in Fig. 6, when the polymeric precursor was synthesized from a mixture of EOPA and 30 mol% acetic acid. The product at 500 °C was amorphous to X-rays, and crystallized in γ-alumina after heat treatment at 800 °C for 1 h (Fig. 6a). DTA–TG analysis of the precursor showed an exothermic peak at 840 °C due to the crystallization of γ-alumina. Fig. 6b and c show that γ-alumina began to transform to α-alumina between 950 and 1000 °C. The crystallinity of α-alumina increased with increasing heat-treatment temperature from 1000–1300 °C as shown in Fig. 6c and d.

3.3.2. *Conversion of polymer fibre to ceramic fibre*

Polymer fibres were spun from the viscous precursor at 35 °C, and then fired in air above 800 °C.

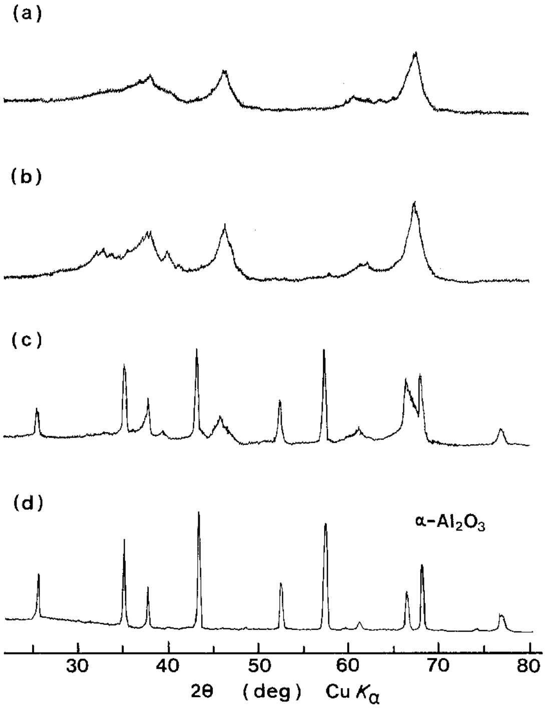


Figure 6 X-ray diffraction profile of alumina after heat treatment between 800 and 1300 °C. (a) 800 °C for 1 h, (b) 950 °C for 1 h, (c) 1000 °C for 1 h, (d) 1300 °C for 1 h.

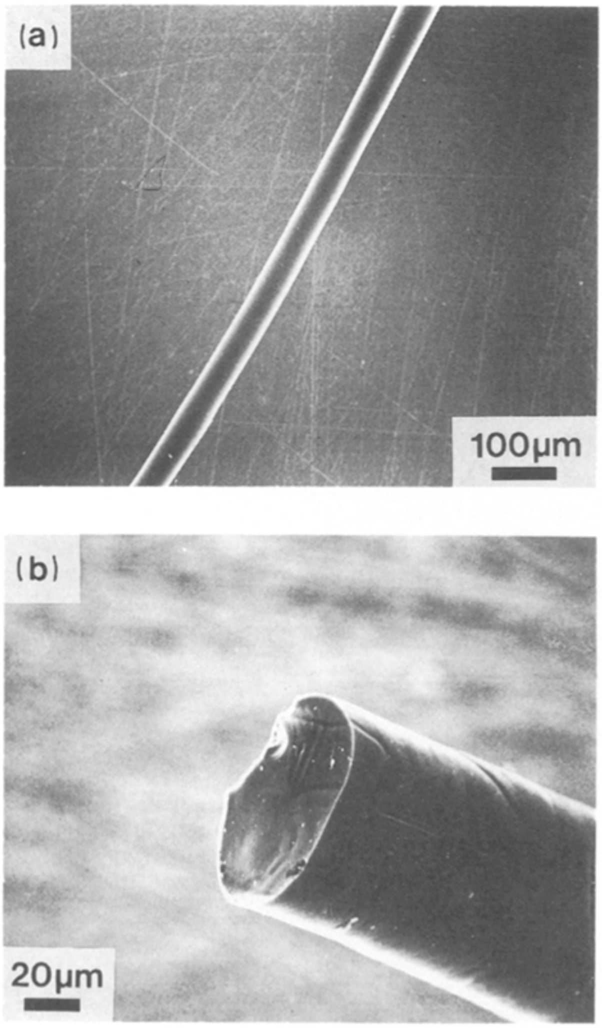


Figure 7 Scanning electron micrographs of alumina fibres: (a) 800 °C for 1 h, (b) 1300 °C for 1 h.

Alumina fibres synthesized from the polymer fibres at 800 and 1300 °C for 1 h are shown in Fig. 7a and b, respectively. The disruption-free fibre was synthesized from the organoaluminium fibre. The diameter of the fibre ranged from 20–100 µm. The fibre surface appeared smooth after heat treatment at 1300 °C for 1 h. No pores were observed in the cross-section, as shown in Fig. 7b.

4. Conclusions

Alumina fibre was synthesized successfully from aluminium chelate precursor without the addition of polymer for the adjustment of viscosity. The results are summarized as follows.

1. Ethyl 3-oxobutanoatodiisopropoxyaluminium was reacted with glacial acetic acid yielding the viscous precursor for alumina fibre.
2. The polymeric product was a mixture of chelate compounds and oligomers, and had a molecular weight below 1000.
3. The higher coordination number of the aluminium atom in the product than that of the starting EOPA results in an increased viscosity.
4. The viscosity of the bulk polymer was independent of time, and was controlled by the selection of temperature in order to obtain an appropriate viscosity for spinning.
5. The preceramic fibre melt-spun from the polymeric precursor was converted to α-alumina fibre with uniform and fine grain size after heat treatment at 1300 °C.

References

1. J. E. BLAZE Jr, US Pat. 3 322 865 (1967).
2. A. BORER and G. P. KRONGSENG, Ger. Offen. 2 210 288 (1972).
3. M. J. MORTON, J. D. BIRCHALL and J. E. CASSIDY, Brit. Pat. 1 360 199 (1974).
4. J. D. BIRCHALL, *Trans. J. Br. Ceram. Soc.* **82** (1983) 143.
5. S. HORIKIRI, Y. ABE and N. TACHIKAWA, *Jpn Pat.* 76 55 429 (1976).
6. S. HORIKIRI, K. TSUJI, Y. ABE, A. FUKUI and E. ICHIKI, Ger. Offen. 2 408 122 (1974).
7. T. R. PATTERSON, F. J. PAVLIK, A. A. BALDONI and R. L. FRANK, *J. Amer. Chem. Soc.* **81** (1959) 4213.
8. C. G. BARRACLOUGH, D. C. BRADLEY, J. LEWIS and I. M. THOMAS, *J. Chem. Soc.* (1961) 2601.
9. R. JAIN, A. K. KAI and R. C. MEHROTRA, *Polyhedron* **5** (1986) 1017.
10. E. BREITMAIER and W. VOELTER, "Carbon-13 NMR Spectroscopy" (VCH, New York, 1987) pp. 208, 218.
11. J. W. AKITT and A. FARTHING, *J. Chem. Soc. Dalt. Trans.* (1981) 1624.
12. O. KRIZ, B. CASENSKY, A. LYCKA, J. FUSEK and S. HARTMANEK, *J. Magn. Reson.* **60** (1984) 375.
13. S. J. KARLIK, E. TARIEN, G. A. ELGAVISH and G. L. EICHHORN, *Inorg. Chem.* **22** (1983) 525.
14. J. W. AKITT and A. FARTHING, *J. Chem. Soc. Dalt. Trans.* (1981) 1615.
15. J. W. AKITT, *Ann. Rep. NMR Spectrosc.* **5A** (1974) 465.

Received 14 September 1990
and accepted 24 January 1991